

Effects of SEI on Lithium Intercalation Kinetics

B. V. Ratnakumar, M. C. Smart and S. Surampudi

*Jet propulsion Laboratory, California Institute of Technology
Pasadena, California*



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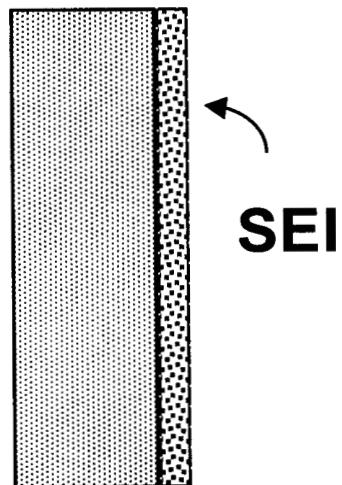
“Solid Electrolyte Interface” (SEI) on Carbon

Impact on Cell Performance

- Specific Capacity
- Irreversible Capacity
- Rate Capability
- Low Temperature Performance
- Cycle Life Performance
- Self-Discharge Properties

Properties

- Nature of composition
- Morphology
- Ionic Resistivity
- Reactivity



Possible Surface Species

- Li_2CO_3
- Li_2O
- Li-O-R
- Li-OCO-R
- LiF

Factors Affecting Formation

- Solvent Type
- Electrolyte Salt Type
- Carbon Type
- Properties of Carbon
- Rate of Formation
- Temperature of Formation

Characterization

- Intercalation Behavior
- AC Impedance
- DC Polarization
- NMR
- In-Situ Techniques (FT-IR)
- Elemental Analysis

Effects of the Carbon SEI on Li Intercalation Kinetics

- **Li Intercalation on SEI-covered electrodes involves**
 - **Charging of the SEI layer**
 - **Charge transfer, more likely at the electrode/film interface due to the ionically conducting film.**
 - **Film (ionic) polarization critical**
 - **Mass transfer either through the SEI or in the bulk of the anode, which are indistinguishable**
 - **Solution mass transfer processes are relatively fast.**

Approaches for Enhanced Low Temperature Performance

- **Improved electrodes**
 - Electrodes with high lithium diffusivity
 - Electrodes with enhanced surface area (Low particle size)
- **Modification of electrolytes**
 - Multi-component systems with low-viscosity species for improved low temperature conductivity
 - Solvents that would form protective (against solvent reduction) and conductive films
 - Current approach with a co-solvent additive to the ‘filming’ carbonate system.
- **Our results indicate that the low temperature is performance controlled by the SEI characteristics more than the ionic mobility in solution.**

Experimental Details

- Three Electrode Half cells
 - KS 44 or MCMB graphite anodes
 - Glass cells (0.5 Ah) with Li counter and reference electrodes
- Three electrode prototype cells with LiCoO_2 or $\text{Li}(\text{Ni}_{1-x}\text{Co}_x)\text{O}_2$ electrodes
- Sealed AA, D or DD cells
- Experimental techniques
 - Charge-discharge capacity measurements and cycling
 - DC polarization techniques (Linear and Tafel)
 - EIS (Electrochemical Impedance Spectroscopy)
 - ${}^7\text{Li}$ NMR
 - XRD and TEM

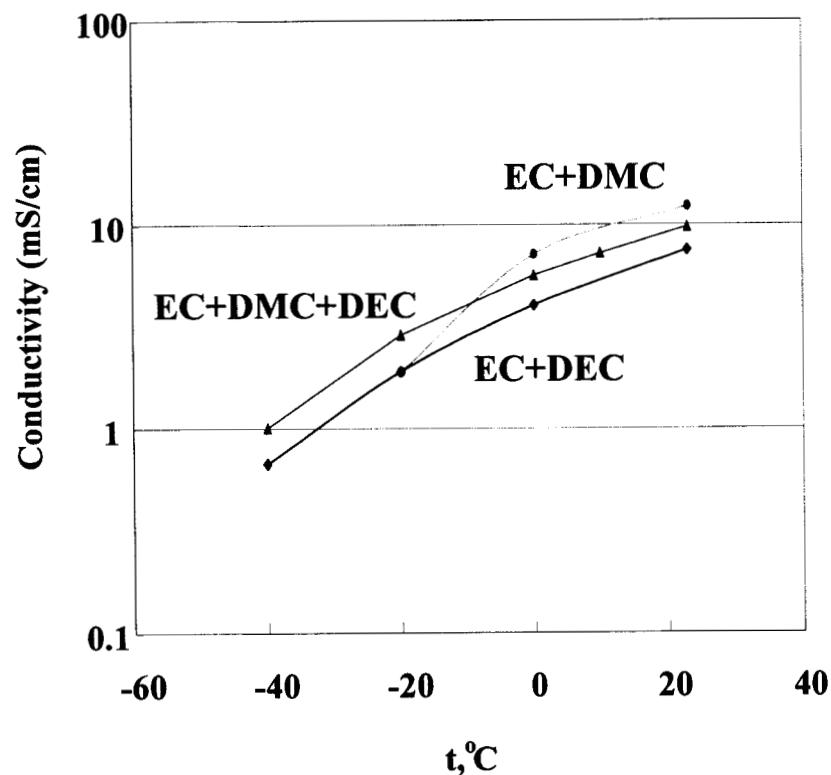
Electrolyte Systems Studied

- Binary mixtures of EC+ DMC and EC+DEC and ternary mixture of EC+DMC+DEC (1:1:1)
- Apliphatic Ester cosolvents to the ternary EC+DMC+DEC (1:1:1) mixtures
 - EC+DMC+DEC+Methyl Acetate (1:1:1+1)
 - EC+DMC+DEC+Ethyl Acetate (1:1:1+1)
 - EC+DMC+DEC+Ethyl Propionate (1:1:1+1)
 - EC+DMC+DEC+Ethyl Butyrate (1:1:1+1)
- Pyrocarbonate additives to the ternary EC+DMC+DEC (1:1:1) mixtures
 - EC+DMC+DEC(1:1:1)+ Dimethyl Pyrocarbonate (5%)
 - EC+DMC+DEC(1:1:1)+ Dibutyl Pyrocarbonate (5%)
- Asymmetric carbonate as co-solvents to the ternary EC+DMC+DEC (1:1:1) mixtures

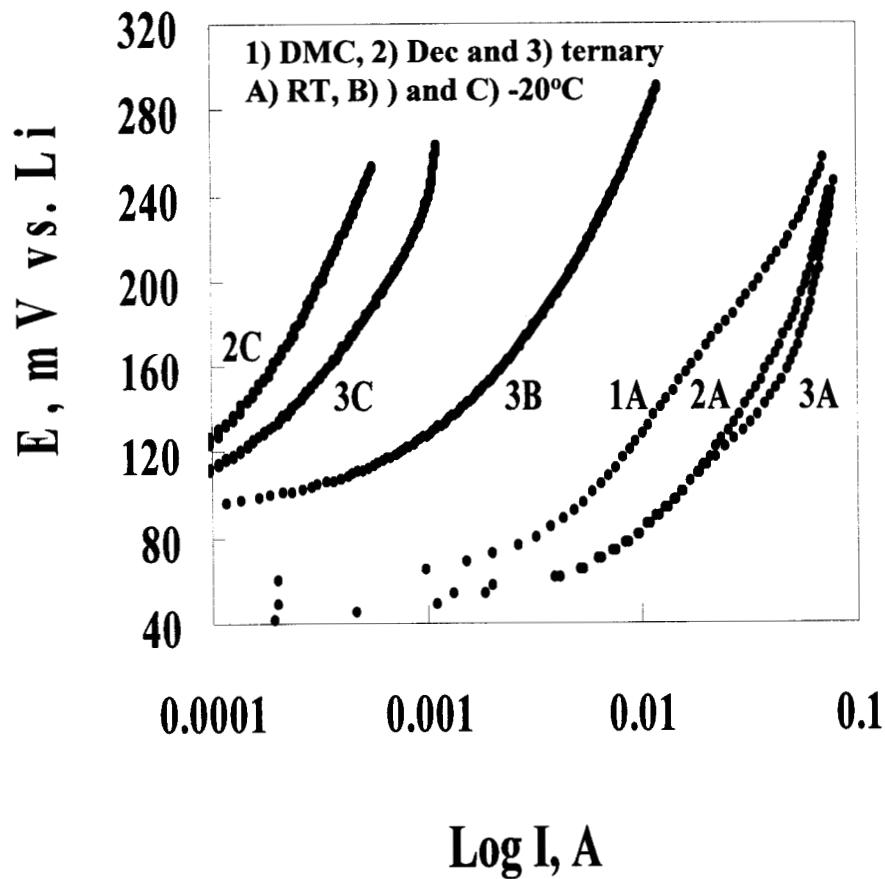
Binary vs. Ternary Carbonate Mixtures

(EC+DMC, EC+DEC and EC+DMC+DEC)

Ionic Conductivity



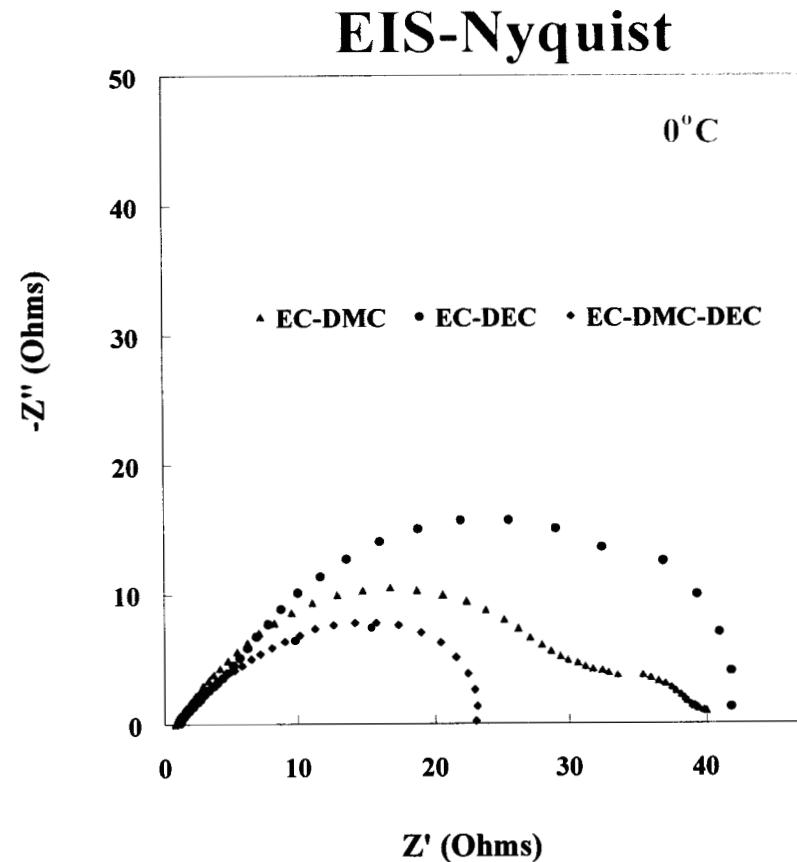
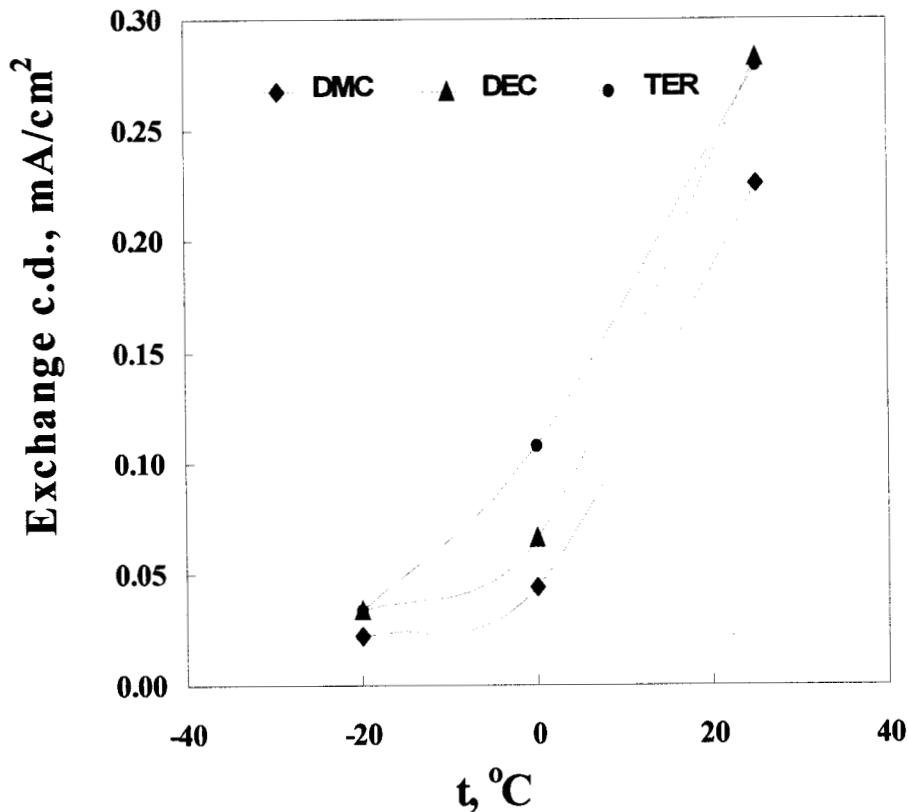
Kinetics-Tafel



- Conductivity and kinetics of the ternary mixture better than the binary mixtures.

Binary vs. Ternary Carbonate Mixtures (EC+DMC, EC+DEC and EC+DMC+DEC)

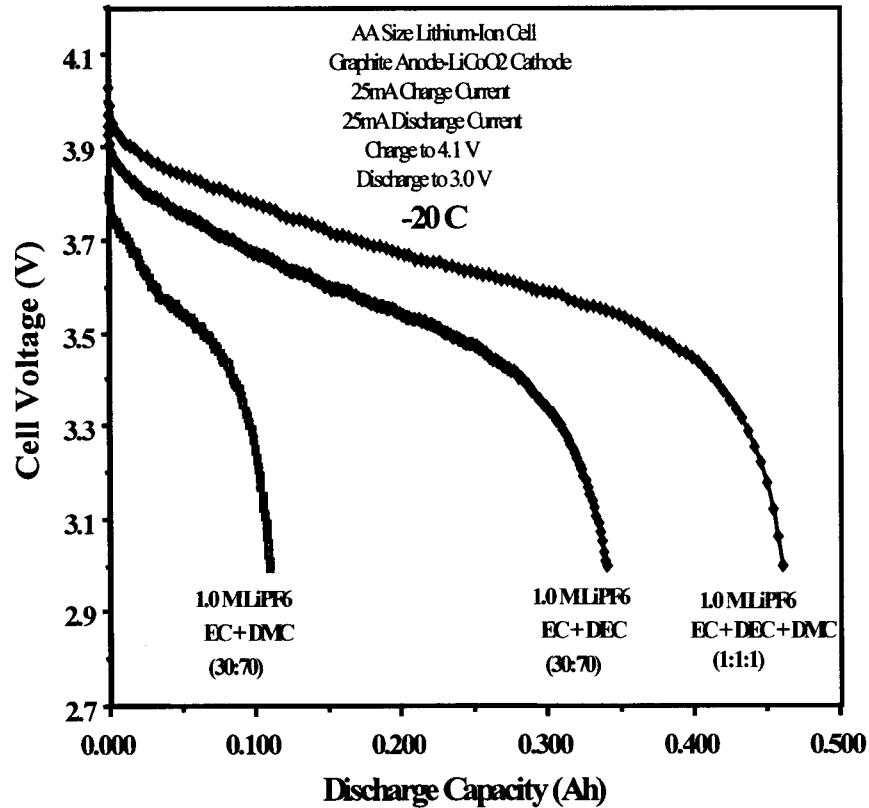
Kinetics from μ -polarization



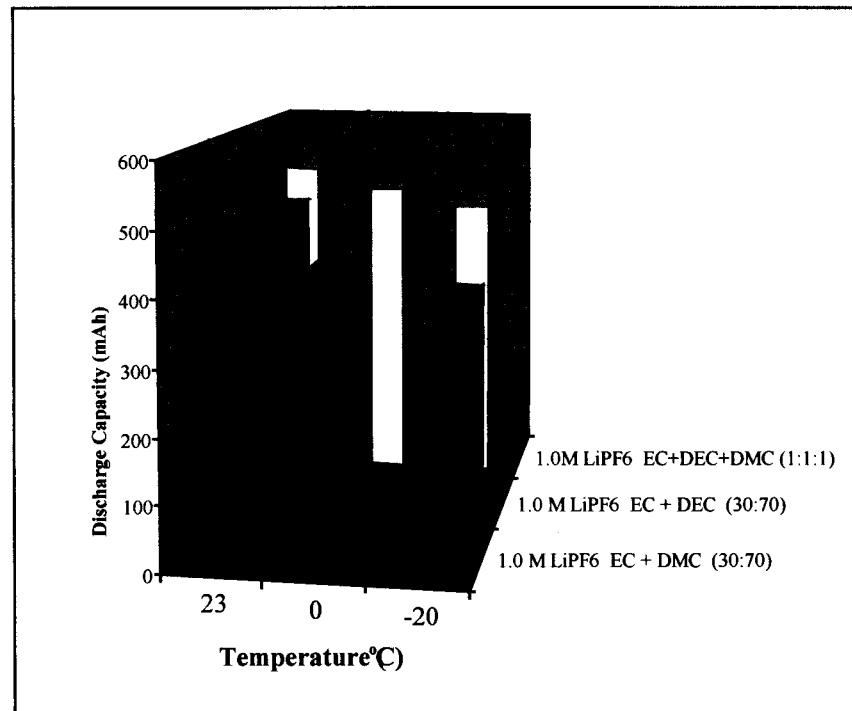
- Kinetics vary as EC+DMC>EC+DMC+DEC+DEC

Binary vs. Ternary Carbonate Mixtures (EC+DMC, EC+DEC and EC+DMC+DEC)

LT Performance



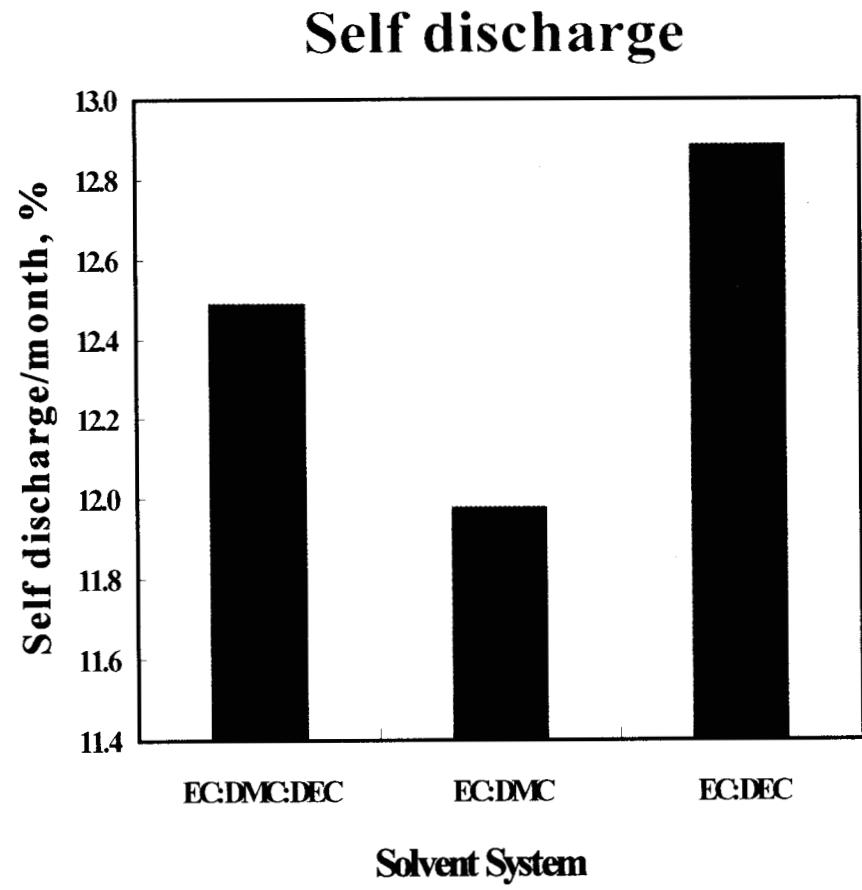
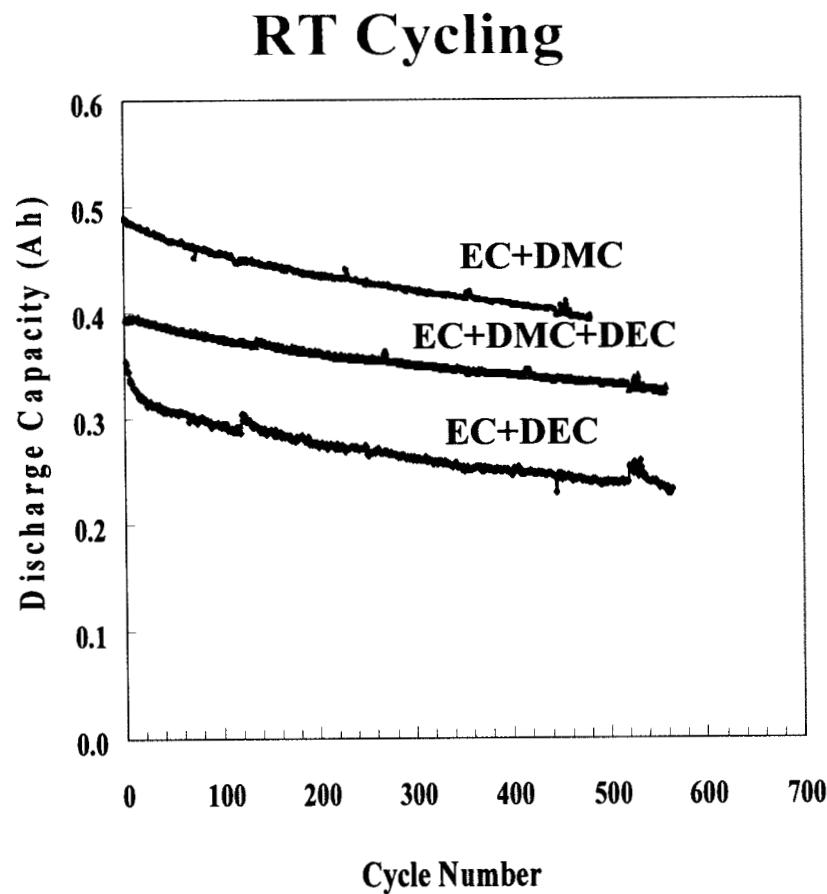
Capacity vs. T



- Improved low temperature performance in the ternary, compared to the binary solvent solutions.

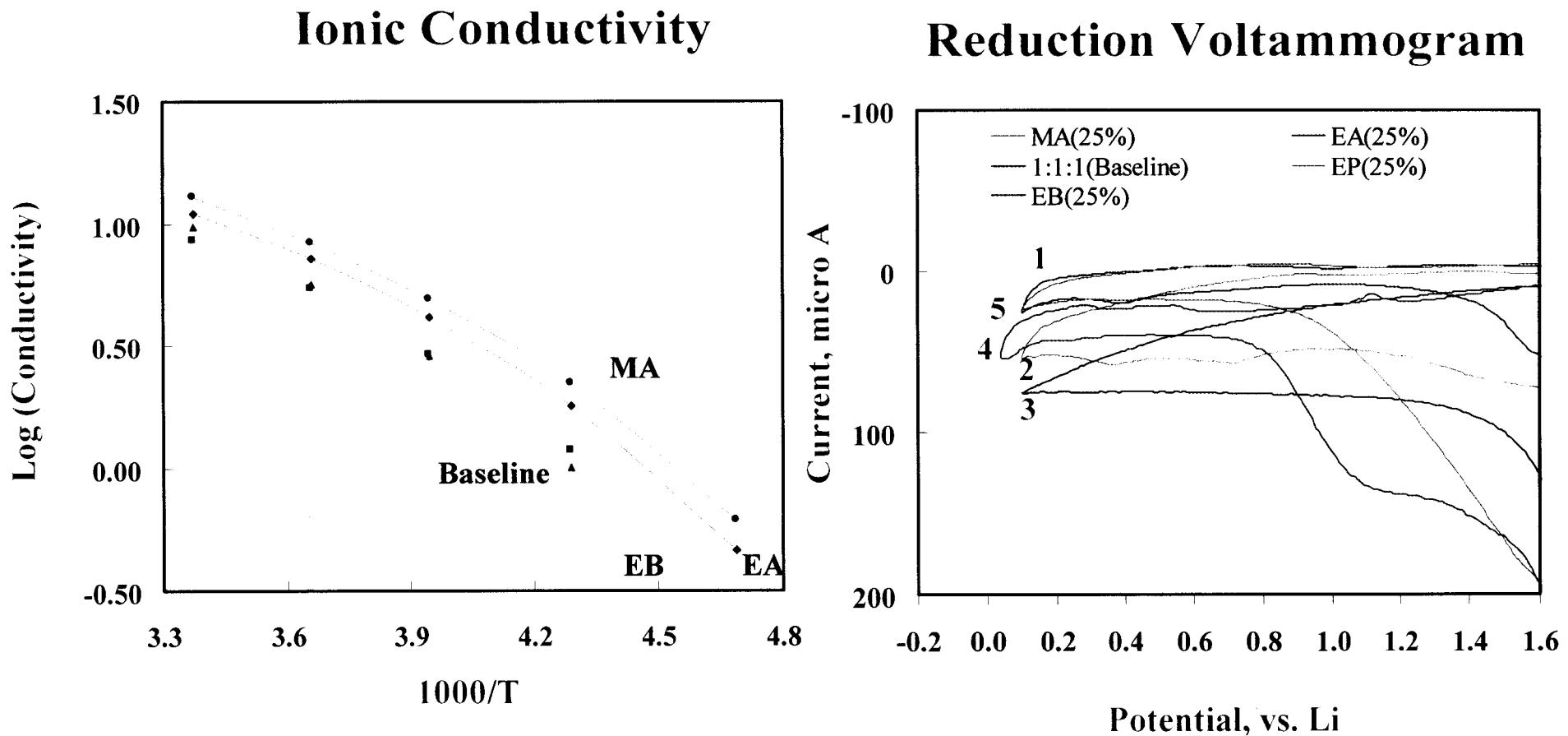
Binary vs. Ternary Carbonate Mixtures

(EC+DMC, EC+DEC and EC+DMC+DEC)



- Cyclic and On-stand stability vary as EC+DMC>EC+DMC+DEC>EC+DEC

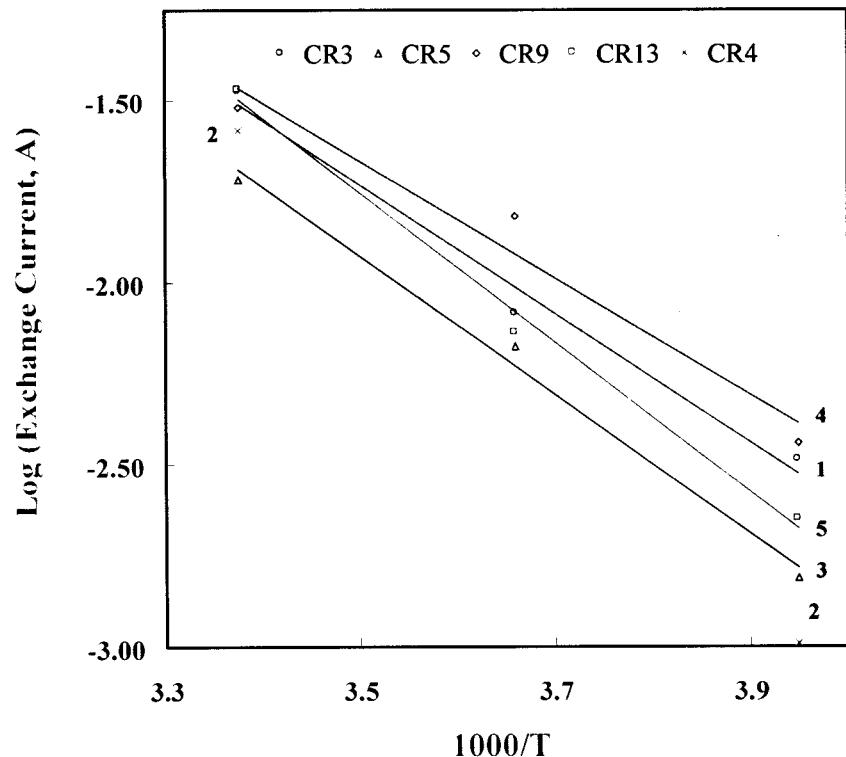
Aliphatic Esters Co-solvents to EC+DMC+DEC



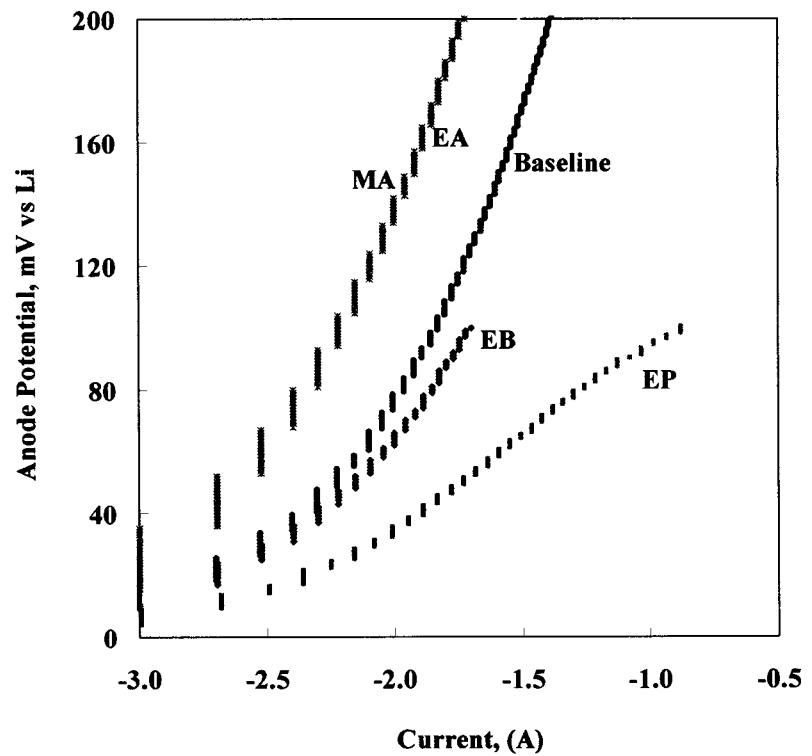
- **Conductivity decreases but reductive stability improves with higher molecular weight esters.**

Aliphatic Esters Co-solvents to EC+DMC+DEC

Kinetics from μ -polarization

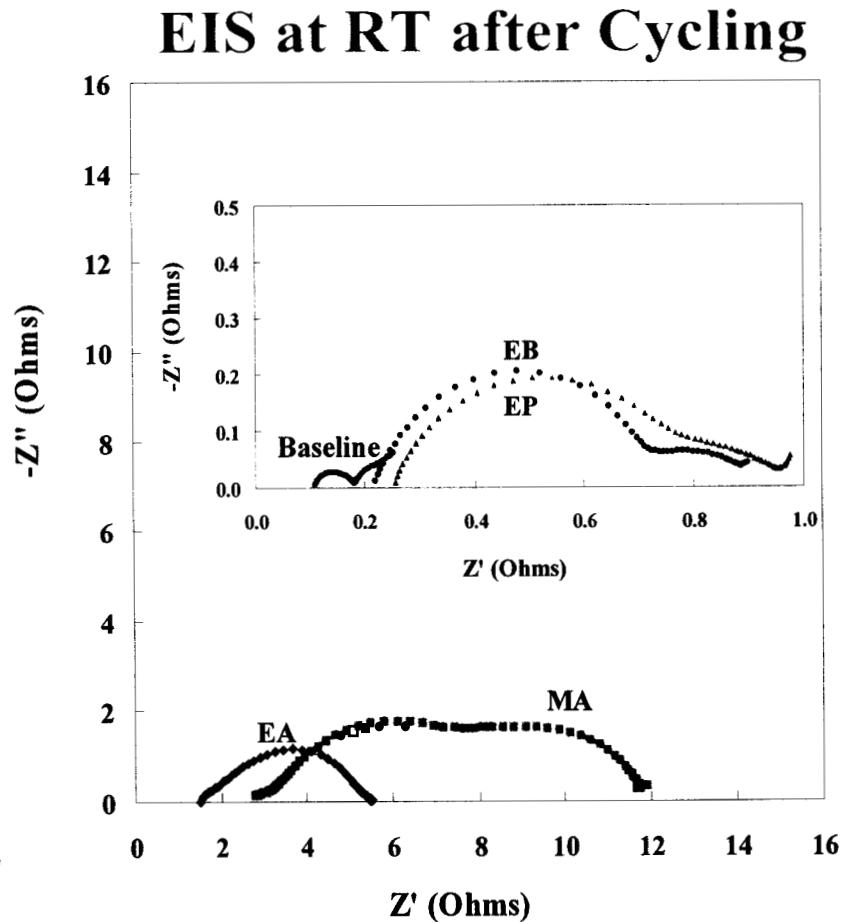
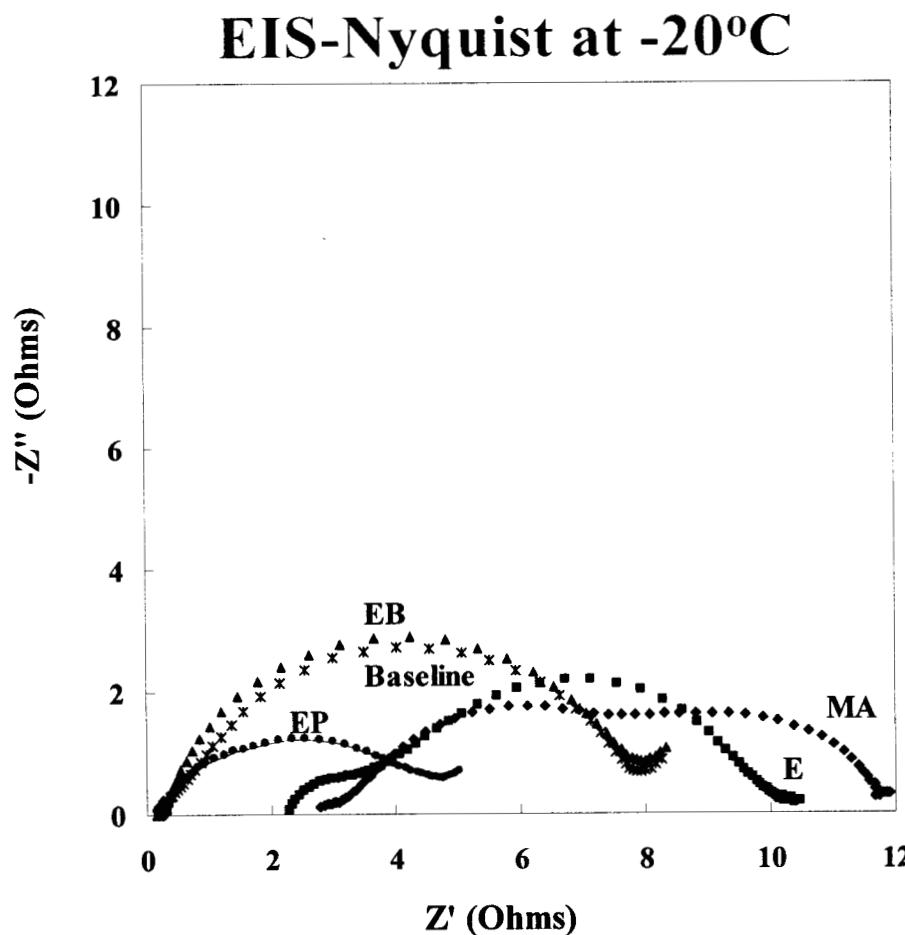


Kinetics from Tafel



- Intercalation kinetics improves with higher molecular weight esters.

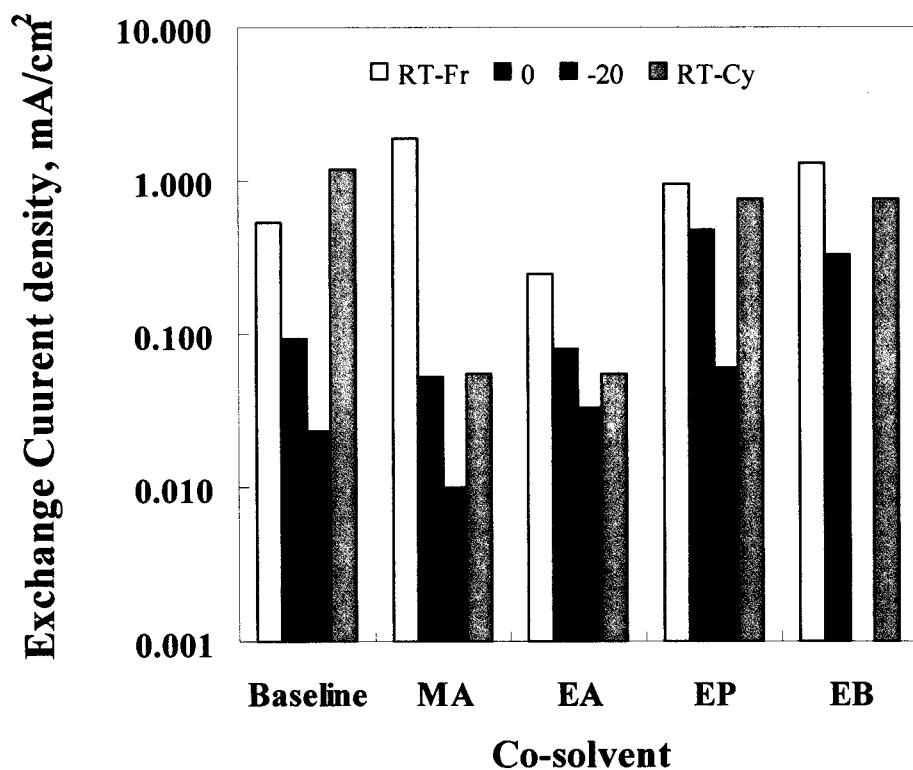
Aliphatic Esters Co-solvents to EC+DMC+DEC



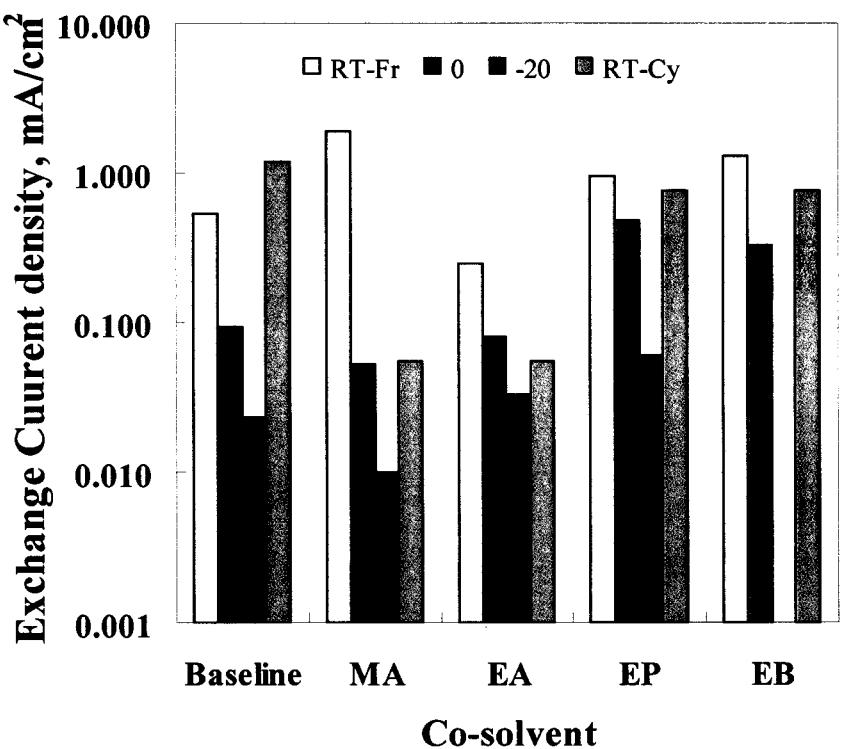
- Interfacial stability improves as **MA<EA<EP≤EB**

Aliphatic Esters Co-solvents to EC+DMC+DEC

Series Resistance



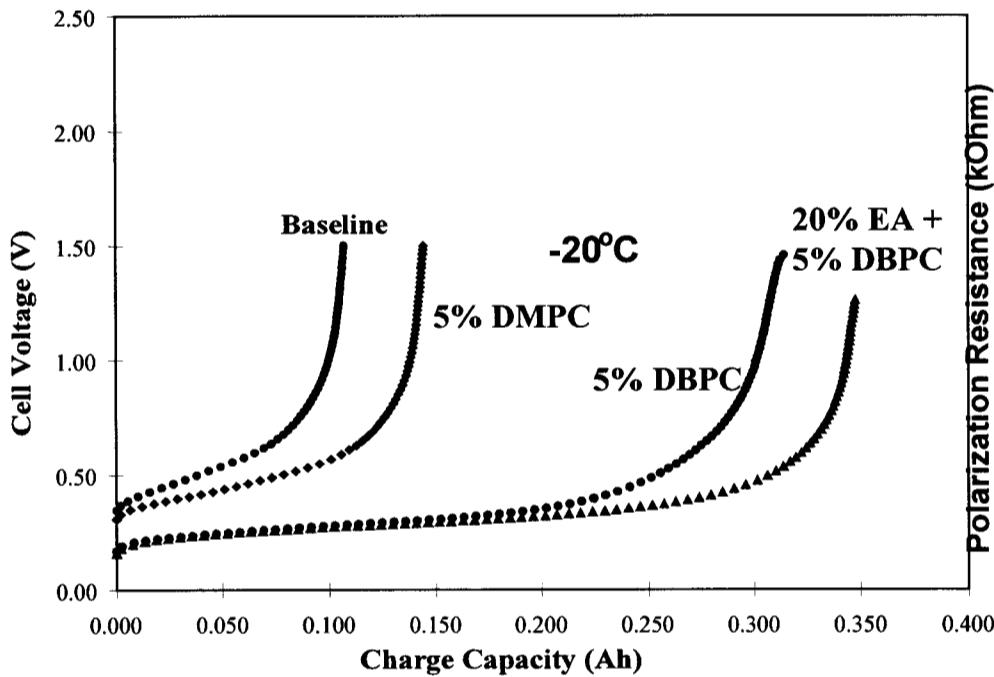
Ch. Transfer Kinetics-EIS



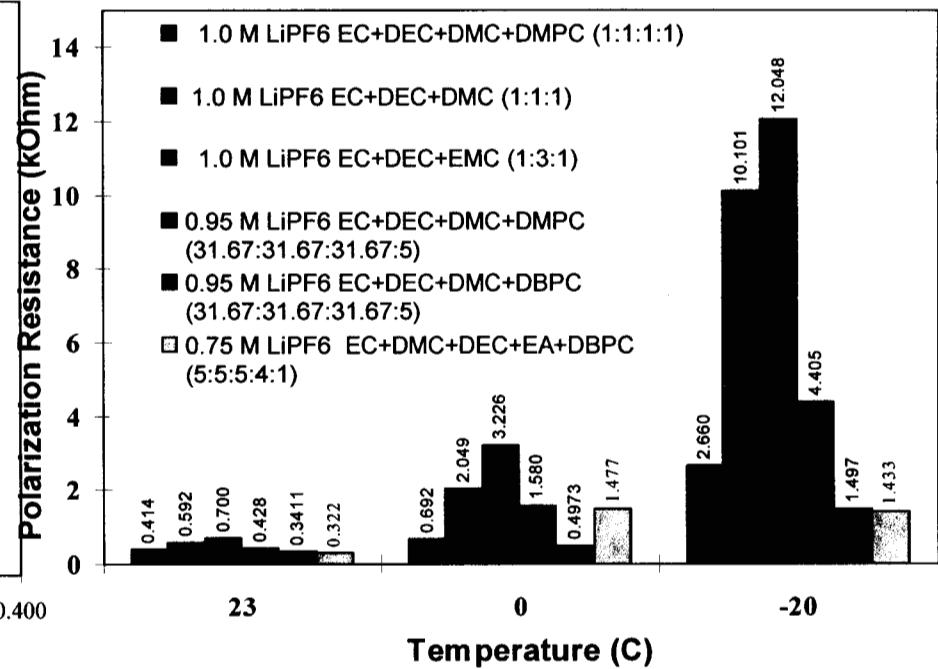
- **Interfacial stability improves with high molecular weight esters.**

Alkyl Pyrocarbonate Additives to EC+DMC+DEC

LT Performance



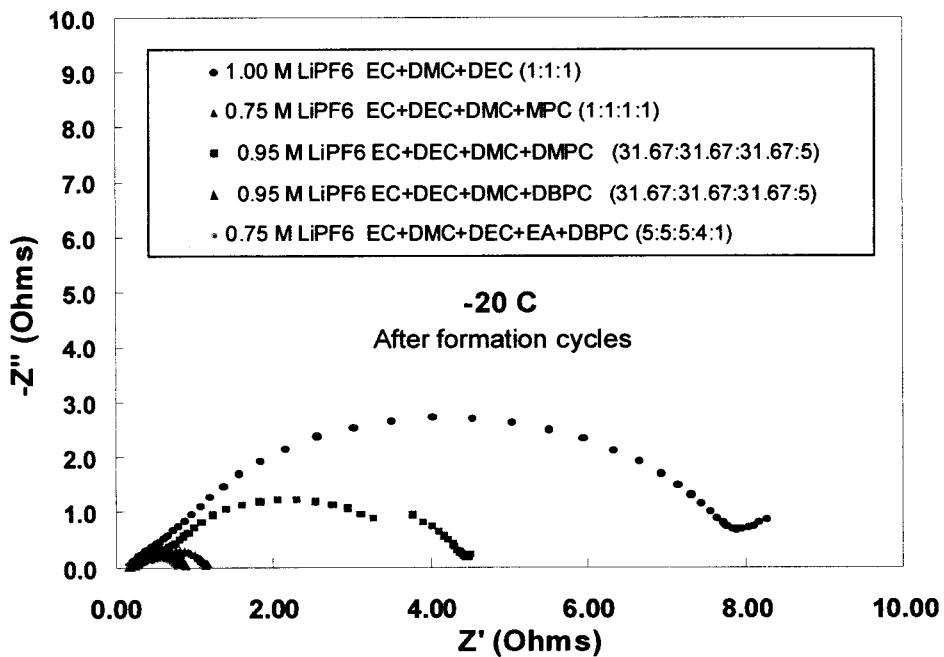
Kinetics from μ -polarization



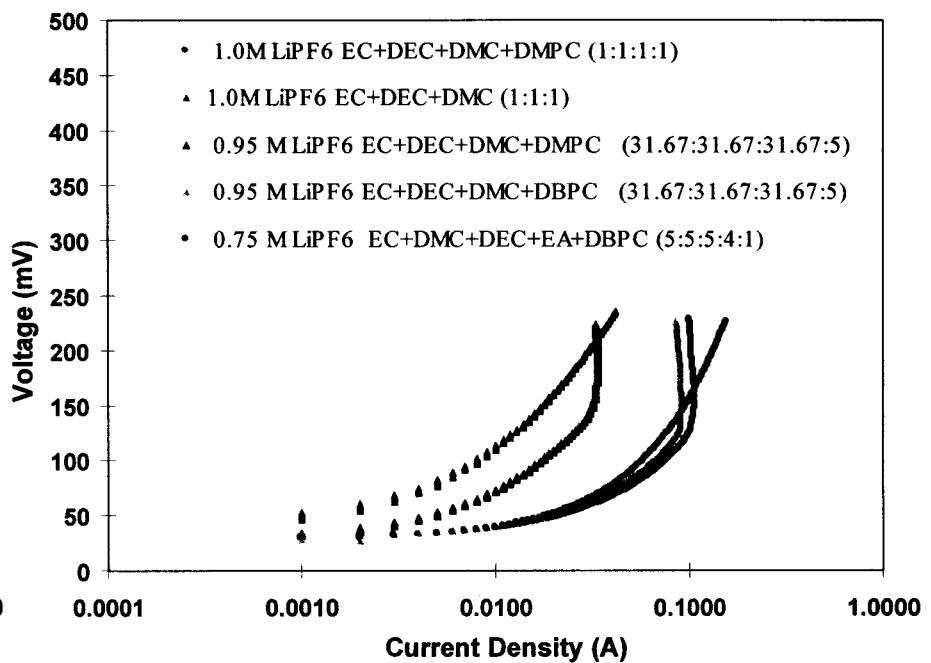
- Low temperature performance significantly improved with 5% addition of pyrocarbonate to the electrolyte.

Alkyl Pyrocarbonate Additives to EC+DMC+DEC

EIS-Nyquist at -20°C



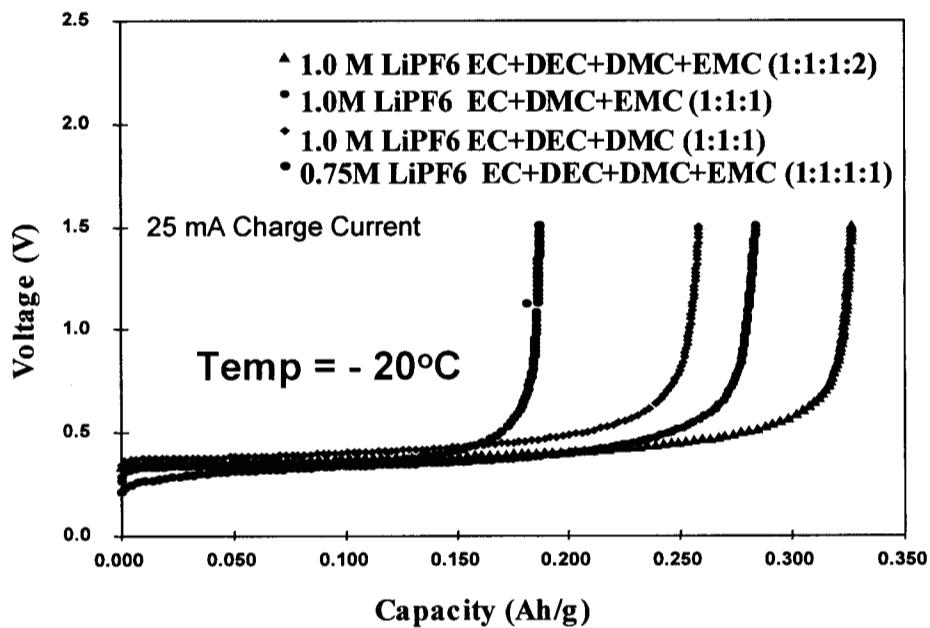
Kinetics from Tafel



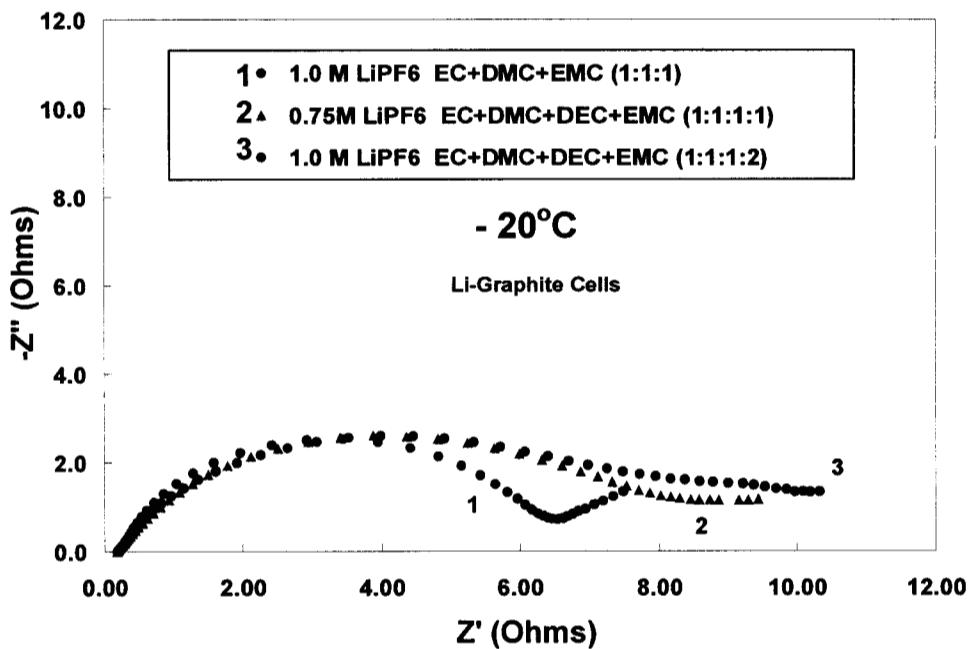
- **Low interfacial resistance and faster kinetics with pyrocarbonate additives.**

Asymmetric Carbonate Co-solvent to EC+DMC+DEC

LT Performance



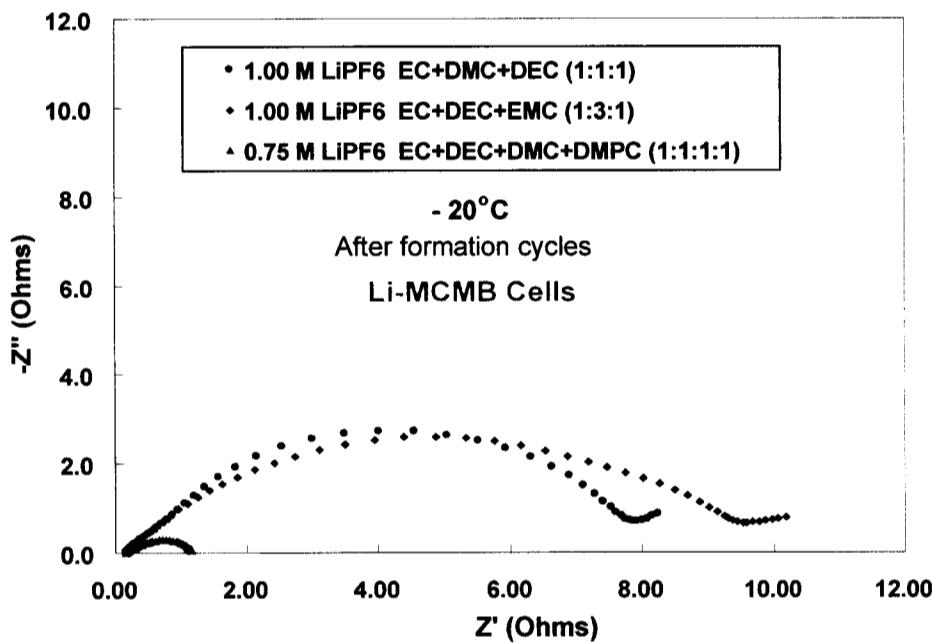
EIS-Nyquist



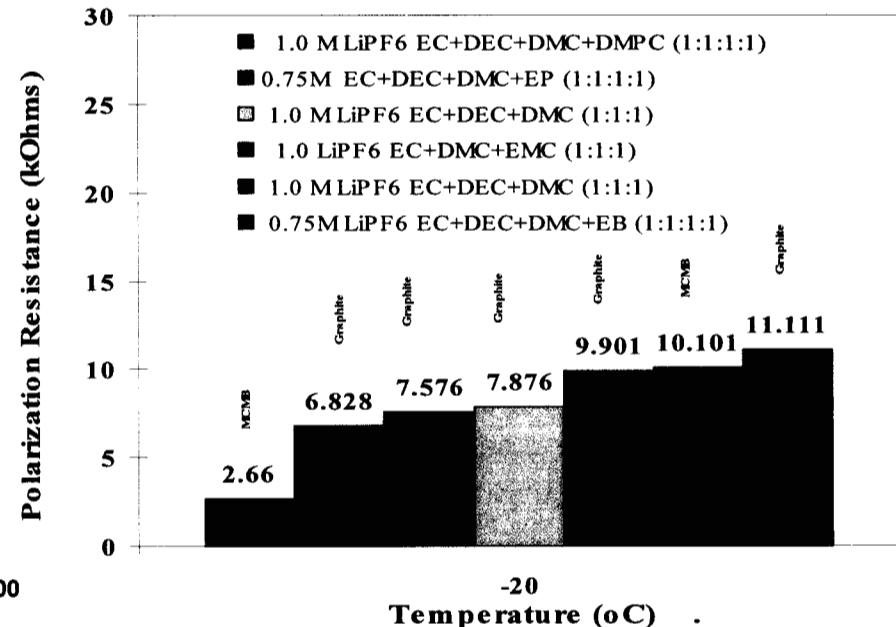
- **Nearly identical behavior (in performance and kinetics with both ternary mixtures**

Co-solvents/additives to EC+DMC+DEC (or EMC)

EIS-Nyquist



LT Kinetics from μ -pol.



- The SEI formed in solutions containing pyrocarbonate is the most amenable for charge transfer at low temperatures.

CONCLUSIONS

- **The ternary formulations provide SEI with more desirable properties for charge transfer at low temperatures.**
- **Ester co-solvents to the ternary mixtures improve the LT performance, by facilitating lithium intercalation. High molecular weight esters form less conductive solutions and yet outperform the low molecular analogues.**
- **Small additions of alkyl pyrocarbonates improve the SEI and considerably enhance the LT performance.**
- **Asymmetric carbonates have good filming properties and thus would be excellent candidates for improving the electrolyte conductivity and the interfacial resistance.**
- **Interfacial conditions (SEI) on the carbon are critical to achieving improvements in the LT performance, probably more than the ion mobility in solutions.**

Acknowledgments

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